Russian Chemical Bulletin 2009 vol.58 N5, pages 908-919

Electron transfer and subsequent reactions during electrochemical oxidation of aryl- and alkylthio derivatives of mucochloric acid

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Abstract

The electrochemical oxidation of aryl- and alkylthio derivatives of mucochloric acid (3,4-dichlor--5-hydroxyfuran-2(5H)-one) in MeCN-Bu 4NBF4 (0.1 mol L-1) was investigated. It was shown that all sulfides are electrochemically active, from one to five oxidation steps of sulfur-containing groups were observed for them. The ease and direction of oxidation of the thio group depend on its nature and position in the furanone ring. 3-Substituted 2(5H)-furanones possess the lowest oxidation potential. 4-Substituted 2(5H)-furanones are predominantly oxidized to sulfoxides, 5-aryl- and -alkylthio derivatives undergo fragmentation to give mucochloric acid, and 3-arylthio derivative gives complex unidentified mixture of products. In the case of 3,4-bis(--methylphenylthio) derivative, the oxidation product of the arylthio group at the 3 position to the corresponding sulfoxide was isolated. Based on the data from cyclic voltammetry with different concentrations of a substrate and water added, the results of preparative electrolysis and quantum chemical calculations, possible mechanisms of electrochemical oxidation of mucochloric acid-derived sulfides are discussed. The initial common step is a reversible single-electron transfer from the substrate molecule to form highly reactive radical cation.

http://dx.doi.org/10.1007/s11172-009-0114-3

Keywords

Electrochemical oxidation, Fragmentation, Furan-2(5H)-ones, Mucochloric acid, Quantum chemistry, Sulfides, Sulfoxide